

# Emissions of formaldehyde, acetic acid, methanol, and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectroscopy

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**Abstract.** Biomass burning is an important source of many trace gases in the global troposphere. We have constructed an airborne trace gas measurement system consisting of a Fourier transform infrared spectrometer (FTIR) coupled to a “flow-through” multipass cell (AFTIR) and installed it on a U. S. Department of Agriculture Forest Service King Air B-90. The first measurements with the new system were conducted in North Carolina during April 1997 on large, isolated biomass fire plumes. Simultaneous measurements included Global Positioning System (GPS); airborne sonde; particle light scattering, CO, and CO<sub>2</sub>; and integrated filter and canister samples. AFTIR spectra acquired within a few kilometers of the fires yielded excess mixing ratios for 10 of the most common trace gases in the smoke: water, carbon dioxide, carbon monoxide, methane, formaldehyde, acetic acid, formic acid, methanol, ethylene, and ammonia. Emission ratios to carbon monoxide for formaldehyde, acetic acid, and methanol were each  $2.5 \pm 1\%$ . This is in excellent agreement with (and confirms the relevance of) our results from laboratory fires. However, these ratios are significantly higher than the emission ratios reported for these compounds in some previous studies of “fresh” smoke. We present a simple photochemical model calculation that suggests that oxygenated organic compounds should be included in the assessment of ozone formation in smoke plumes. Our measured emission factors indicate that biomass fires could account for a significant portion of the oxygenated organic compounds and HO<sub>x</sub> present in the tropical troposphere during the dry season. Our fire measurements, along with recent measurements of oxygenated biogenic emissions and oxygenated organic compounds in the free troposphere, indicate that these rarely measured compounds play a major, but poorly understood, role in the HO<sub>x</sub>, NO<sub>x</sub>, and O<sub>3</sub> chemistry of the troposphere.

## 1. Introduction

Biomass burning can be a useful land management practice [Wade and Lunsford, 1989], a natural and beneficial part of the ecology of the world's seasonally dry forests and grasslands [Muich, 1994], a key component of important agricultural systems [Steinhart and Steinhart, 1974; Jordan, 1985], and an enormous potential source of renewable energy [Brink et al., 1976]. Biomass burning is also a significant source of atmospheric trace gases and particles [Crutzen and Andreae, 1990]. Uncertainty in the initial characteristics and the subsequent transformations of these emissions is a major limiting factor in models of atmospheric chemistry, radiative transfer, and global climate change [Crutzen and Carmichael, 1993; Kaufman and Nakajima, 1993; Prather et al., 1994]. Airborne studies have quantified some of the important

atmospheric impacts that result from individual fires [Nance et al., 1993] or that occur over large regions where many different types of fires burn simultaneously [Andreae et al., 1988, 1994; Lindesay et al., 1996]. The field work of several investigators [Ward et al., 1992, 1996] has helped clarify how the different types of fuels and burning conditions, associated with specific land use practices, affect the initial emissions of particles, CO<sub>2</sub>, CO, and hydrocarbons. Laboratory studies of simulated fires have provided measurements of the initial emissions for many compounds, including some containing nitrogen or halogens [Lobert et al., 1991; Kuhlbusch et al., 1991].

We have carried out a series of laboratory studies designed to give an overview of fire emissions that has exploited the high accuracy possible in the laboratory environment and the advantages of open-path Fourier transform infrared spectroscopy (OP-FTIR) [Yokelson et al., 1996b, 1997, 1999; Goode et al., 1999]. The advantages of OP-FTIR included the ability to make continuous, smoke-plume-integrated, low-interference measurements of nearly any reactive or stable gas present at, or above, mixing ratios of a few parts per billion by volume (ppbv). In the laboratory we made OP-FTIR measurements of the major emissions generated by the different combustion processes throughout fires in well-characterized fuels. These emissions included carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>), formaldehyde (HCHO), hydroxyacetaldehyde (CH<sub>2</sub>OHCHO),

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~8-11 m in height. The dead biomass was very dry for this region (5-9% moisture), which accounts for the high estimated fuel loading of 18 t/ha. The sky was clear, and temperature and relative humidity were 19.5°C and 38%, respectively. The wind was generally from the west and less than 8 m/s. The fire started before 1400 EST and spread intermittently at average rates up to ~3 m/min (occasionally torching individual trees). The maximum, average flame length was ~3 m and about 80% of the estimated fuel consumption of 11 t/ha occurred in the flame front. The fire burned about 24 ha by 1815. We obtained one AFTIR sample from this fire, which coincided with a less active period when only a faint column of (mainly) smoldering emissions was present.

**2.1.3. Camp Lejeune fire 2 (CL2): April 26, 1997.** The treatment area was 564 ha containing 281 ha of 50+ year old pine (20-23 m height), 121 ha of hardwood, and 162 ha of annually burned military range. The approximate location was 34.60°N, 77.24°W. The average fuel load estimated before the fire was 11 t/ha. The conditions were the wettest of the three fires with fuel moistures ranging from 8% to 28%. Cloud cover ranged from 0 in the morning to 75% by midafternoon. The temperature and relative humidity ranged from 19°C and 40% (~1000) to 21°C and 37% (1300). The wind speed was 1-4 m/s and varied widely in direction throughout the day. The backfire was started at 0940, and aerial ignition commenced within the next hour using a 23 x 23 m ball spacing. The fire skimmed off the top layer of ground fuels at average spread rates of 0.6 to 2.1 m/min and with average flame lengths up to 2 m. About 182 ha burned with the most active flaming combustion ending by 1300, but pockets of flaming combustion and a convection column persisted until ~1600. The lapse rate was -8.8°C/km in the morning, decreasing to -8.5°C/km in the afternoon, up to an inversion at 2 km. All the samples were taken close to the fire (again due to airspace restrictions) and below 1.7 km.

## 2.2. Measurement Strategy

Many configurations can be used to perform airborne FTIR. Solar, atmospheric, or terrestrial radiation that has passed through a long atmospheric path can be collected and analyzed [Mankin, 1978; Toon *et al.*, 1989; Traub *et al.*, 1994; Worden *et al.*, 1997]. This approach is very powerful, but not ideal for measuring excess combustion emissions that are also present in large quantities in background air, such as CO<sub>2</sub> and methane. Local, external, optical in situ measurements can be made by employing a source (or retroreflector) attached to the aircraft [Webster and May, 1987; Haschberger and Lindermeir, 1996], but this would limit us to a short path length. In this work we coupled an FTIR to a multipass cell inside the aircraft. The system performs in situ measurements by admitting external air into the cell through a sampling line connected to a port on the aircraft exterior. An analogous arrangement has been used for diode laser measurements of ambient atmospheric trace gases [Hastie and Miller, 1985; Sachse *et al.*, 1987; Schiff *et al.*, 1990; Podolske and Loewenstein, 1993; Webster *et al.*, 1994] and by McGee and Gerlach [1998] for FTIR measurements of SO<sub>2</sub> in a volcanic plume. Use of this configuration incurs a small risk of sampling artifacts, which we reduced by coating the intake surfaces with nonreactive halocarbon wax [Webster *et al.*, 1994].

## 2.3. Optical System Design

The Forest Service King Air can support a scientific payload, including passengers, of approximately 800 kg for a 3 hour flight. To accommodate the largest possible selection of instrumentation for smoke plume characterization, a primary design consideration for AFTIR was minimizing size and weight while maximizing the optical path length (proportional to sensitivity). Figure 1 shows a schematic of the AFTIR system. The system is described in detail, as it was configured for the North Carolina flights, below. (Photographs of the system can be found on the World Wide Web (<http://www.cas.unt.edu/chem/yokelson/>).)

The IR beam exiting the spectrometer (MIDAC, Inc.) is steered by transfer optics to a "tripled" white cell (IR Analysis, Inc.) featuring MgF<sub>2</sub>-coated silver mirrors and two retroreflectors mounted inside a 15 (i.d.) X 91 cm Pyrex tube. The variable path cell has a base path of 0.81 m and was passed 120 times for a total path of 97.5 m. Viton O-rings seal the ends of the tube to nickel-plated aluminum endplates. Temperature inside the white cell was measured by a thermocouple at each end, and cell pressure was measured by a capacitive transducer (Kavlico, Inc.). All metal surfaces inside the cell were coated with halocarbon wax to reduce surface reactivity (Halocarbon, Inc.). Mirrors directed the exit beam from the cell through a 25 mm focal length ZnSe lens onto the LN<sub>2</sub>-cooled, "wideband" MCT detector (Graseby, Inc., model FTIR M-16). The MIDAC spectrometer was operated at its maximum spectral resolution of 0.5 cm<sup>-1</sup>. The optical elements of the AFTIR system were mounted on a 28 x 175 x 11 cm, honeycomb core, optical table (Newport, Inc.) that was shock mounted (Aeroflex, Inc.) to the floor of the aircraft. Total system weight including a protective sheet metal shield was approximately 64 kg.

## 2.4. Sample/Flow System

An aluminum plate was built to temporarily replace the copilot's vent window upon which forward facing aluminum elbows were mounted to serve as sample inlets. The AFTIR inlet was 25 mm i.d. and was wax coated as described above. Approximately 1.5 m of 17 mm i.d. (wax-coated) Teflon tubing connected the aircraft sample inlet to the multipass cell inlet located near the top of the front endplate. A deflector attached to the inside of the front endplate served to deflect the incoming gas stream into a circular pattern behind the field mirror. The gas then flowed slowly through large notches in the field mirror and through the cell to an outlet near the bottom of the back endplate. Manual 15 mm i.d. ball valves (wax-coated) provided flow control for the inlet and outlet lines. Use of the valves allowed us to perform in situ measurements of the cell exchange time by opening the valves in clean air after "grabbing" a sample in a smoke plume. The 1/e exchange time was typically 7-8 s (considerably longer than the 1.7 s spectrometer scan speed) and limited our spatial accuracy to ~700 m at the King Air sampling speed of 90 m/s.

The optical throughput of the AFTIR system and the spectrum of background air were constantly monitored throughout the experiment to check for a variety of potential problems, including cell contamination. The throughput (when measured at a pressure of ~1 atm) did not vary significantly throughout the study. The background spectra did not show any noticeable features indicating a buildup of

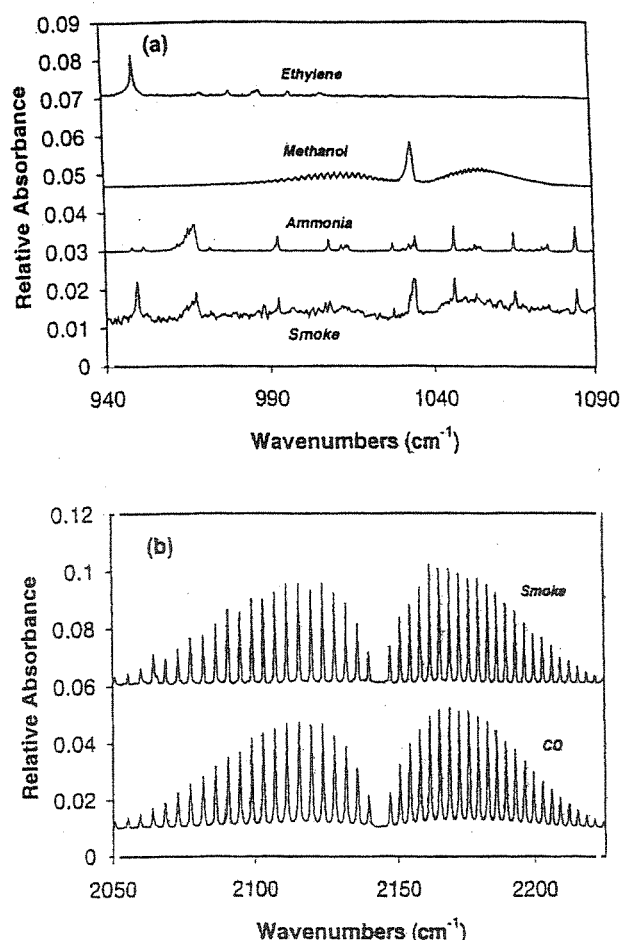


Figure 2. Two regions of an AFTIR absorbance spectrum. (a) The spectral region used to quantify ethylene, methanol, and ammonia, along with the reference spectra for these compounds. Water is also included in the spectral subtraction protocol for this region. (b) The spectral region around 2100  $\text{cm}^{-1}$  along with a reference spectrum of CO to illustrate the excellent SNR for this compound. (Actual quantification is done with the transmission spectrum as explained in the text. The effects of water lines, which are fit simultaneously in the CLS analysis, explain the "extra" or distorted features in the smoke spectrum.)

made by using background sample spectra obtained at nearly the same altitude, and these were analyzed by spectral subtraction [Yokelson *et al.*, 1997] to yield mixing ratios for  $\text{H}_2\text{O}$ ,  $\text{HCOOH}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_3$ ,  $\text{C}_2\text{H}_4$ , and  $\text{CH}_3\text{OH}$ . Figure 2a shows part of an AFTIR smoke absorption spectrum along with reference spectra for the three latter compounds. Figure 2b shows another portion of the same smoke absorption spectrum, along with a CO reference spectrum, to illustrate the high SNR for this important combustion tracer. For this application we developed programs to efficiently perform these mixing ratio retrievals for large numbers of spectra acquired at many different temperatures and pressures.

For ammonia only, a modified data analysis protocol was followed as discussed next. Several smoke storage tests conducted in the cell (in our laboratory) showed ammonia and all the other species to be sufficiently stable to justify signal averaging for the 1–10 min time periods that samples were stored in the field. (Species  $1/e$  lifetimes were typically > 10

hours.) However, at the lower smoke concentrations actually encountered in the field, ammonia, and ammonia only, showed evidence of a decay during the time grab samples were held. The decay had a  $1/e$  lifetime of about 35 s. We investigated this decay as follows. We used detailed formulas given by Perry *et al.*, [1963] to calculate the diffusion coefficient for ammonia in air and obtained  $0.282 \text{ cm}^2/\text{s}$ . We then used this value of  $D(\text{NH}_3/\text{air})$  in a formula given by McDaniel [1964] to calculate the diffusion-limited, first-order wall-loss lifetime for a species in a cylinder of known dimensions. The theoretical ammonia lifetime due to wall loss limited by radial diffusion, in our cell, was 35 s. Thus we conclude that the observed decay seems consistent with a first-order wall loss. Accordingly, for the ammonia analysis, the smoke sample scans were analyzed at higher time resolution, and the mixing ratios were then back-corrected to "time zero" assuming a first-order decay. We ignored  $\text{NH}_3$  values below 20 ppb because of the extra error introduced by the back-correction and the reduced SNR at higher time resolution. A plot of  $\text{NH}_3$  versus CO for the CL2 fire is shown in Figure 3. The plot indicates that our approach is yielding fairly consistent results.

In this type of airborne plume sampling, the mixing ratio in a measurement is not always the absolute mixing ratio at a known point in the plume. We compute the difference between similarly collected samples of the plume and background air to obtain and report "excess mixing ratios." However, it is the arithmetic ratios between the excess mixing ratios that are the most meaningful quantity (especially ratios to excess CO, which is the best short-term smoke tracer).

The accuracy of the excess mixing ratios measured in this experiment is mainly determined by the SNR of the spectra and by uncertainty in the spectroscopic cross sections and sample density measurements. The last type of error should tend to cancel when measuring ratios between compounds, the quantity of most interest here. The rms noise level in the spectra acquired in North Carolina is < 0.001 absorbance units for a 1 min signal-averaging period. Thus the detection limits (which vary by compound and spectrum) were typically from 5 to 20 ppbv (SNR=1). The spectroscopic cross sections are estimated to be accurate to  $\pm 5\%$  [Rothman *et al.*, 1992; Hanst and Hanst, 1994]. The relative density of the background and smoke samples was resolved to about  $\pm 5\%$ . The residual from the CLS fit or subtraction routine is < 5%. Thus the

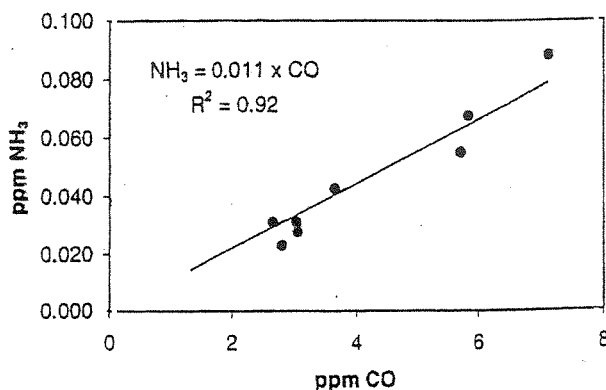


Figure 3. Excess ammonia mixing ratios for the CL2 fire, obtained by the method described in the text, plotted against the simultaneously measured excess mixing ratios for CO.

Table 2. Excess Mixing Ratios Determined by AFTIR and Sample Time and Location for the CL2 fire on April 26, 1997, and the Single Sample for the Wildfire on April 19, 1997

Sample	Altitude, m	Time, EST	CO <sub>2</sub> , Δppmv	CO, Δppmv	CH <sub>4</sub> , Δppmv	HCHO, Δppmv	NH <sub>3</sub> , Δppmv	CH <sub>3</sub> OH, Δppmv	HCOOH, Δppmv	CH <sub>3</sub> COOH, Δppmv	C <sub>2</sub> H <sub>4</sub> , Δppmv
s01	84	10:24	45.8	2.79	0.494	0.059	0.023	0.048	0.021	0.059	0.044
s02	133	10:38	100.8	7.15	0.643	0.203	0.088	0.158	0.059	0.109	0.136
s03	208	10:46	44.6	3.05	0.427	0.077	0.027	0.072	0.026	0.058	0.054
s04	327	10:48	39.7	3.03	0.448	0.076	0.031	0.066	0.011	0.086	0.049
s05	457	10:50	18.6	1.54	0.291	0.058		0.038		0.035	0.019
s06	598	10:52	29.4	2.65	0.420	0.097	0.031	0.057	0.036	0.075	0.052
s07	692	10:54	21.0	1.59	0.343	0.042		0.035	0.033	0.030	0.022
s08	796	10:57	11.0	1.31	0.215	0.039		0.031	0.020	0.026	0.019
s09	1031	10:59	19.4	2.48	0.201	0.065		0.062	0.009	0.060	0.024
s10	995	11:11	13.3	1.81	0.209	0.045		0.041	0.028	0.016	0.026
s11	215	11:40	59.8	5.83	0.589	0.144	0.068	0.128	0.050	0.140	0.102
s12	154	11:51	42.0	3.65	0.407	0.107	0.042	0.074	0.032	0.062	0.049
s14	120	14:40	74.6	5.71	0.520	0.131	0.055	0.135		0.060	0.054
s16	268	15:37	57.0	5.06	0.413	0.114		0.084		0.046	0.055
s17	122	15:53	35.8	2.66	0.382	0.056		0.022	0.014	0.063	
Intercompound Ratios											
Value based on slope			CO/CO <sub>2</sub>	CH <sub>4</sub> /CO	HCHO/CO	NH <sub>3</sub> /CO	CH <sub>3</sub> OH/CO	HCOOH/CO	CH <sub>3</sub> CO <sub>2</sub> H/CO	C <sub>2</sub> H <sub>4</sub> /CO	
R <sup>2</sup>			0.079	0.108	0.0258	0.0110	0.0211	0.0085	0.0173	0.0150	
			0.89	0.24	0.91	0.92	0.90	0.50	0.45	0.79	
Emission factors, g/kg			CO <sub>2</sub>	CH <sub>4</sub>	HCHO	NH <sub>3</sub>	CH <sub>3</sub> OH	HCOOH	CH <sub>3</sub> COOH	C <sub>2</sub> H <sub>4</sub>	
Combustion efficiency			1671	5.18	2.32	0.56	2.03	1.17	3.11	1.26	
Modified combustion efficiency			0.907								
			0.927								
Sample from wildfire 1, Δppmv											
Ratio to CO			CO		HCHO	NH <sub>3</sub>	CH <sub>3</sub> OH	HCOOH	CH <sub>3</sub> COOH	C <sub>2</sub> H <sub>4</sub>	
			2.93		0.096	0.077	0.071	0.035	0.050	0.040	
					0.033	0.026	0.024	0.012	0.017	0.014	

The sample for wildfire 1 was at an altitude of 267 m and was taken at 16:40 EST.

resulting values were within a few percent of those obtained using the other methods described above. *Little and Rubin* [1987] discussed estimating ratios between measured quantities when a data set has some missing values, as is the case in a few instances in this study. They concluded that the best estimate of the ratio is the slope of the least squares line, with the intercept forced to zero, in a plot of one set of measurements versus the other. The fire-average emission ratios shown in Tables 1 and 2 are computed in this way, though, as we showed above, essentially the same result is obtained by the three other methods.

For the CL1 and CL2 fires we measured a suite of the major carbon-containing fire emissions. Thus we can calculate an approximate emission factor for any species "i" using

$$EF_i(\text{g/kg}) = F_c \times 1000(\text{g/kg}) \times \frac{MM_i(\text{g})}{12(\text{g})} \times \frac{C_i}{C_T} \quad (1)$$

In equation (1),  $EF_i$  is the mass (g) of compound  $i$  emitted per kg of fuel burned,  $F_c$  is the mass fraction of carbon in the fuel, and  $MM_i$  is the molecular mass of species  $i$ .  $C_i/C_T$  is the number of moles emitted of species  $i$  divided by the total number of moles of carbon emitted.  $C_i/C_T$  can be calculated from an individual, a fire-averaged, or a study-averaged suite of measurements. In this case we wanted the best estimate of fire-average  $C_i/C_T$ , so we calculated this value from fire-average emission ratios using

$$\frac{C_i}{C_T} = \frac{\frac{\Delta C_i}{\Delta \text{CO}_2}}{\sum_{j=1}^n (NC_j \times \frac{\Delta C_j}{\Delta \text{CO}_2})} \quad (2)$$

In equation (2),  $\Delta C_i/\Delta \text{CO}_2$  is the fire-average emission ratio of compound  $i$  to  $\text{CO}_2$ ,  $NC_j$  is the number of carbon atoms in compound  $j$ , and the sum is over all the species (including  $\text{CO}_2$ ). The use of equations (1) and (2) to estimate fire-average emission factors is most accurate when all the burnt carbon is volatilized and detected, the fraction of fuel carbon is precisely known, and the measurements probe all the smoke produced by the fire. In this study we probably underestimate the total carbon 1-2% by ignoring particulate and another 1-2% due to unmeasured gases. We also assume that the fuel is 0.5 carbon by mass [*Susott et al.*, 1996], which is probably accurate to  $\pm 10\%$  ( $2\sigma$ ).

Our fire-averaged quantities could also differ from the actual source characteristics if our sampling was unrepresentative. This condition might occur if the plume was changing in composition, poorly mixed, or, for any other reason, not characteristic of the products of the whole fire. These issues are addressed next. In previous ground-based experiments we have learned that as long as flames persist on the site, emissions from the various combustion processes can be drawn into the plume (including smoldering combustion emissions originating some distance from the moving flame fronts) [*Ward et al.*, 1992]. If large amounts of fuel were consumed after convection from the site ceased, then airborne measurements could be in error (if the smoke composition also changed). On the two Camp Lejeune fires for which we report emission factors the amount of postconvection residual smoldering combustion was minimal because the proportion

of large dead fuels was small and any organic soils were too wet to ignite. This was confirmed by direct observation of the burn interior during and after the fire. We have also taken some precautions against poor mixing or changing composition. We acquired a fairly large number of samples (15 or 25), the samples were from many different locations in the plume, the samples integrated over transects through the plume, and they were taken during a large portion of the time that fuel consumption occurred.

For fires CL1 and CL2 the estimates of the fire-average emission factors, the fire-average modified combustion efficiency (MCE), and the fire-average combustion efficiency are shown in Tables 1 and 2. Combustion efficiency (CE) is defined as the fraction of burned carbon that is released as  $\text{CO}_2$ . Modified combustion efficiency is defined as  $\Delta \text{CO}_2/(\Delta \text{CO}_2 + \Delta \text{CO})$ ; where the " $\Delta$ " indicates an excess mixing ratio [*Ward and Radke*, 1993]. MCE is also equal to  $1/((\Delta \text{CO}/\Delta \text{CO}_2) + 1)$ . CE and MCE are useful as indexes of the relative amount of flaming and smoldering combustion throughout (or during) a fire, and these terms are used to compare studies below. The concept of MCE is also important because if our measurements oversampled either flaming or smoldering combustion, the relation obtained between MCE and the emission factors should still be valid.

A full discussion of the emissions of  $\text{CO}_2$ , CO, particles,  $\text{NO}_x$ , and hydrocarbons from these fires, and earlier fires in Florida and Georgia (where the AFTIR was not deployed), will be presented separately. We limit further discussion in this paper to the AFTIR measurements of oxygenated organic compounds (for which much less literature information is available).

### 3.1. Production of Oxygenated Organic Compounds From Biomass Fires

Comparison of measurements of biomass fire emissions between different studies is complicated by the fact that natural fires burn in a wide variety of fuels and environmental conditions and with different relative amounts of flaming and smoldering combustion. Some consideration of the differences between fires can be incorporated into a comparison by plotting emission factors versus modified combustion efficiency (MCE) [*Ward and Radke*, 1993]. These plots give a two-dimensional (2-D) comparison, which is more informative than a simple one-dimensional comparison of emission ratios from potentially very different fires. It is of special interest to use this 2-D plot to compare our current field data for the three main oxygenated organic compounds (HCHO,  $\text{CH}_3\text{COOH}$ , and  $\text{CH}_3\text{OH}$ ) with our previous laboratory data for these compounds. This helps determine how similar the emissions from our laboratory fires are to the emissions from full-scale field fires and could confirm the relevance of our extensive, laboratory fire emissions data for these, and other, compounds.

In three previous laboratory studies [*Yokelson et al.*, 1996b, 1999; *Goode et al.*, 1999] our work included measurements of the fire-integrated emission factors for formaldehyde, methanol, and acetic acid from fires burning in different fuels and at different MCEs. In one previous laboratory study [*Yokelson et al.*, 1997] we measured emission factors and MCEs for smoldering combustion only. In Figure 5 we compare our current field measurements of emission factors (for the dominant oxygenated organic

and 1%, respectively. Further, plotting the data versus  $\Delta\text{CO}/\Delta\text{CO}_2$  gives essentially the same correlation and only a small ( $\sim 1\%$ ) shift in the intercept toward the equivalent of higher MCE fires. Thus the plots appear to be fairly robust models for predicting fire emissions in a wide variety of circumstances with the following caveats. We have no data at an MCE above 0.98 and no points from in situ measurements in tropical fuels. Therefore we plan such measurements in the near future to enable more confident prediction for these scenarios. Meanwhile, the plots can be employed for predicting emissions from temperate zone fires and for preliminary estimates of the emissions from tropical fires. For instance, *Andreae et al.* [1996] reported a global average MCE for tropical savanna fires of 0.94. Employing Figure 5, we obtain average savanna fire emission factors for formaldehyde, methanol, and acetic acid of 1.6, 1.1, and 2.5 g/kg respectively ( $\pm 50\%$ ). *Ward et al.* [1992] reported an average MCE for tropical deforestation fires of 0.89. Employing Figure 5 (a little more confidently in this case), the analogous emission factors for tropical forest fires are considerably higher at 3.8, 2.8, and 6.2 g/kg respectively ( $\pm 30\%$ ). Combining these emission factors with estimates of the amount of biomass burned in savanna and forest fires in the tropics [*Crutzen and Andreae*, 1990] yields emissions of  $14 \pm 8$ ,  $10 \pm 6$ , and  $22 \pm 13$  Tg/yr. It should be recalled that these emissions are concentrated spatially and temporally to a few months during the tropical dry season and that the compounds are too reactive to become well mixed in the global troposphere.

The estimates derived above can be compared on a very limited basis with other estimates. *Singh et al.* [1995] suggested that total global methanol production is  $\sim 45$  Tg/yr based on their methanol measurements in the remote troposphere and they estimated that  $\sim 6$  Tg/yr of this production is due to total global biomass burning. Our calculation suggests a larger fire source of methanol since we obtain  $10 \pm 6$  Tg/yr without including burning of fuel wood and agricultural waste (which may be 10–20% of global biomass burning). Evidently, fires may contribute some 10–30% of global atmospheric methanol. The major source of this compound is probably biogenic emissions [*Konig et al.*, 1995; *Singh et al.*, 1995; *Kirstine et al.*, 1998].

A plot of emission factor versus MCE does not imply that the emission ratio to CO for a compound is constant. In fact, for most smoldering compounds the emission ratio to CO increases as MCE decreases. Thus comparison of emission ratios from two fires with different MCE can be misleading. However, in many studies, and in our measurements of WF1, there is insufficient data to calculate MCE. Therefore examination of emission ratios allows us to compare/integrate data from a larger number of studies, with the limitations just noted. Additionally, comparison of emission ratios is more meaningful if the two compounds in the ratio are from the same type of combustion. Thus comparison of smoldering or pyrolysis compounds to CO is quite useful, especially since CO is a smoldering compound and also the best gas phase tracer for smoke in the field.

In Table 3 we compare our field measurements of the fire-average emission ratios for oxygenated organic compounds to CO with our laboratory study-average emission ratios and to other work. All the measurements were made on different fires, so only a summary comparison of this data is justified. *Talbot et al.* [1988] sampled laboratory fires for

emissions of formic and acetic acid with a mist chamber technique. Their study-average emission ratios to CO for these compounds are about 100 and 20 times lower than ours, respectively. The tendency for their values to be lower than ours holds for a wide range of MCEs, as was seen in Figure 5. *Griffith et al.* [1991] reported that HCHO was a ubiquitous fire product emitted on average at  $\sim 1.3\%$  of CO. (*Lobert et al.* [1991] did not attempt to quantify oxygenated organic compounds in their benchmark study.) *Hurst et al.* [1994] sampled savanna fire smoke in glass bulbs and later analyzed the contents with matrix isolation-FTIR. They reported an average HCHO/CO value of 0.25 that is  $\sim 7$  times lower than our typical value. However, they also reported total aldehyde emissions up to 1.7% of CO. *McKenzie et al.* [1995] packed finely ground biomass into ceramic crucibles and heated it from above. Smoke generated in this manner was cryotrapped and analyzed by gas chromatography-mass spectrometry (GC-MS) for a variety of oxygenated compounds, of which four are also measured in our FTIR work. Their values of HCOOH/CO, CH<sub>3</sub>COOH/CO, and CH<sub>3</sub>OH/CO are 1/4 to 1/2 of our typical values. Their data are not correlated with MCE (see Figure 5), perhaps partly due to the highly stratified biomass they burned [*Yokelson et al.* 1997].

Another airborne FTIR smoke study [*Worden et al.*, 1997] reported values for two spot measurements of HCOOH/CO, CH<sub>3</sub>OH/CO, and NH<sub>3</sub>/CO obtained during smoldering combustion that are well within the range we observed in a study of smoldering combustion [*Yokelson et al.* 1997]. Recently, *Holzinger et al.* [1999] used a chemical ionization mass spectrometer for on-line emissions measurements of six trace gases from laboratory fires. Their average value for HCHO/CO (2.2%) is essentially the same as ours. Their average value for CH<sub>3</sub>OH/CO (0.64%) is about 1/3 of our typical FTIR value. Finally, *Koppmann et al.* [1997] used absorption tube/GC-MS to measure many high-molecular-mass organic emissions from savanna fires in southern Africa. They reported that the oxygenated compounds were approximately equal to the straight hydrocarbons in abundance. This is consistent with our findings for the lighter C<sub>1</sub> and C<sub>2</sub> hydrocarbons as indicated in the footnote to Table 3. In summary, consideration of the published measurements of the ratio of oxygenated organic compounds to CO supports our earlier conclusion that fires are a major source of these compounds.

### 3.2. Influence of Oxygenated Organic Compounds on Initial Plume Chemistry

In this section we briefly summarize some of the published results relevant to "smoke chemistry" and then, in the context of this previous work, we demonstrate that oxygenated compounds may play an important, but poorly understood, role in early plume chemistry. Trace gas emissions from biomass fires have many important influences on the atmosphere. This includes emission of 10–30% of global CO and significant amounts of greenhouse gases [*Crutzen and Andreae*, 1990]. Another important topic is the influence of fires on tropospheric O<sub>3</sub> formation [*Chatfield and Delaney*, 1990; *Fishman et al.*, 1991; *Richardson et al.*, 1991; *Keller et al.*, 1991; *Jacob et al.*, 1992; *Crutzen and Carmichael*, 1993; *Chatfield et al.*, 1996; *Thompson et al.*, 1996; *Jacob et al.*, 1996; *Koppmann et al.*, 1997; *Lelieveld et al.*, 1997; *Olson et al.*, 1997; *Mauzerall et al.*, 1998; *Lee et al.*, 1998]. About 80–90% of the global biomass burning is estimated to occur in

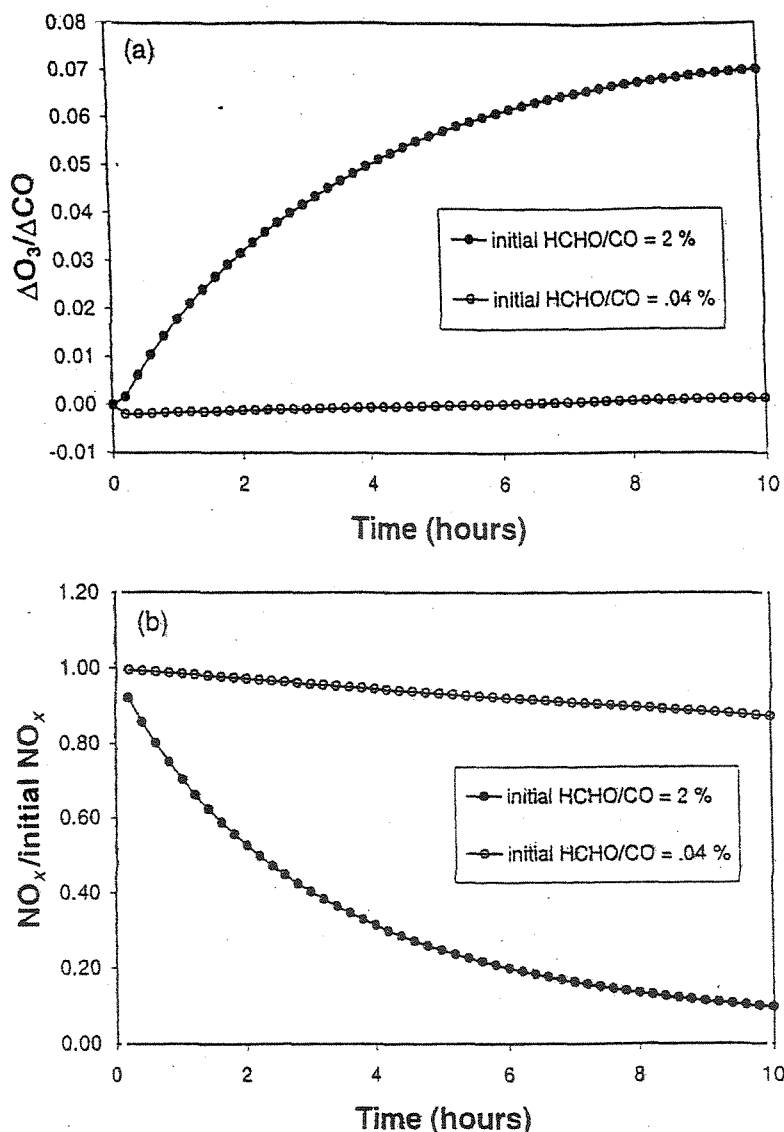


Figure 6. Results are shown for  $O_3$  production and  $NO_x$  depletion from paired runs of a simple smoke chemistry model. For each plot, one run sets the initial  $HCHO$  at background levels and the other run sets the initial  $HCHO$  at 2% of the initial  $CO$  (see Table 3). (a) The excess  $O_3$  mixing ratio divided by the excess  $CO$  mixing ratio (a common measure of ozone production). (b) The  $NO_x$  mixing ratio divided by its initial value of 80 ppbv. The differences between the runs are examples of how increased, modeled rates of initial (near source)  $O_3$  formation and  $NO_x$  depletion can result from including oxygenated organic compounds in a simple chemical system. Initial mixing ratios for the model runs were:  $CO$ , 7.7 ppm (total including 0.2 ppm background);  $CH_4$ , 2.3 ppm (total including 1.7 ppm background);  $NO$ , 60 ppb (total);  $NO_2$ , 20 ppb (total); and  $O_3$ , 30 ppb (total).  $HCHO$  was varied as indicated above.

the tropics [Hao and Liu, 1994]. Further, since the tropical troposphere is where most of the oxidation in the atmosphere occurs, tropical tropospheric ozone has a major influence on the oxidizing capacity of the global atmosphere [Cruzen and Carmichael, 1993].  $O_3$  is also the third most important greenhouse gas (after  $CO_2$  and methane) [Prather et al., 1994], with tropical upper tropospheric  $O_3$  being especially effective in this respect [Fishman et al., 1979]. Using a global three-dimensional chemistry-transport model, Lelieveld et al. [1997] estimated that fires cause a 15% increase in tropical  $O_3$  (lower limit) and concluded that most of this  $O_3$  increase appears to be due to regional-scale production from dispersed biomass burning emissions. High regional production is

inferred partly because of the great increase in modeled  $O_3$  formation rates that follows convective transport of "fresh" biomass burning emissions (still containing ample  $NO_x$ ) to the upper troposphere [Chatfield and Delaney, 1990; Pickering et al., 1992; Thompson et al., 1996; Jacob et al., 1996; Lelieveld et al., 1997]. Thus the rate of the chemistry and the transport of the smoke can interact in ways that greatly affect the amount of ozone produced.

Many modeling studies have examined ozone formation in biomass burning plumes, but to our knowledge, none have incorporated a suite of low-molecular-weight oxygenated organic compounds in the initial emissions as our (and other's) work clearly suggests is appropriate. In light of this



and ethylene), the rarely quantified oxygenated organic compounds (formaldehyde, methanol, acetic acid, and formic acid), and ammonia. The results confirm the importance of biomass fires as a source of oxygenated organic compounds, and a simple model suggests that these compounds will affect the rate of  $O_3$  formation in biomass burning plumes. The results also suggest that fires will contribute to the ambient levels of  $HO_x$  and oxygenated organic compounds in the upper troposphere. The agreement between our field results and our previous laboratory results confirms the relevance of our extensive work characterizing emissions from modeled laboratory fires.

**Acknowledgments.** This research was supported by the National Science Foundation under grants ATM-9631219 and ATM-9900494, by the Rocky Mountain Research Station, Forest Service, U. S. Department of Agriculture (INT-96079-RJVA and INT-97082-RJVA), and by funds provided by Camp Lejeune Marine Corps Base (MIPR M6700195MP47041). The authors have the pleasure of thanking many people who contributed to the timely and successful first deployment of the prototype AFTIR system. We thank Tim Johnson (Bruker Inc.), Frank Murcay (University of Denver), Glen Sachse (NASA Langley), Randy Webster (JPL), Jim Kendall (JPL), and others for enlightening discussions on their experience with optical systems and airborne sampling. Mike Chandler of RMRS and Mike Huey of the Forest Service Equipment Development Center assisted in building the transfer optics and other apparatus. The staff of the Forest Service Aviation and Fire Management office in Missoula arranged for our use of the Forest Service King Air. Bob Nichols was our expert pilot. Peter Black and Daniel Becker of the Environmental Management Department of Camp Lejeune and James Cherry of the Croatan National Forest carried out the controlled burns and arranged our entry into Camp Lejeune airspace.

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(Received February 16, 1999; revised July 9, 1999;  
accepted August 6, 1999.)